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Laboratory Notes from the University of Cincinnati.

## XXVII.—ON SOME PHOSPHIDES OF IRIDIUM AND PLATINUM.

BY F. W. CLARKE AND O. T. JOSLIN.

In May, 1881, Mr. John Holland, a manufacturer of gold pens in Cincinnati, took out a patent for a process of fusing iridosmine. For pointing gold pens, only selected grains of the native mineral were suitable; and his object was to utilise the quantities of unavailable mineral which accumulated in his establishment. His process, briefly stated, consisted in heating the ore to whiteness, and then throwing in upon it common phosphorus; fusion at once took place, and the excess of phosphorus was afterwards removed by heating the product in contact with lime. The metal thus produced was harder than steel, brilliantly lustrous, insoluble in acids, and available for a great variety of purposes. As the process has already been fully described by Professor W. L. Dudley,<sup>1</sup> it needs no further technical discussion here. Our work relates to the chemical side of the new iridium industry.

At an early date, samples of the "fused iridium" were placed in our hands for examination, together with some of the original ore from which the melts had been made. The latter was a Californian iridosmine, in hard, brilliant grains, of specific gravity 19.182. Of the fused product the sp. gr. was only 13.768.

<sup>1</sup> Sci. Proc. Ohio Mechanics Institute, Jan., 1882.

Two portions of the latter were prepared at different times, for comparison with the native mineral, and partial analyses were made. In the first portion, phosphorus only was determined, three estimations giving respectively 7.52, 7.58, and 7.74 per cent. This portion contained barely a trace of osmium.

In the iridosmine itself 15.38 per cent. of osmium were found; and accordingly the second fused portion was examined with special reference to this element. As far as it was carried out, the analysis gave the following results:

Iridium,	80.82
Osmium,	6.95
Phosphorus,	7.09
Ruthenium and Rhodium,	7.20
	<hr/>
	102.06

No attempt was made to separate the ruthenium and rhodium, nor to trace out the cause of the plus error. The phosphorus agrees reasonably well with the estimations made in the first portion; and the low percentage for osmium, compared with the mere trace in the other lot and the large amount in the ore, shows that this element is more or less eliminated according to the circumstances attending fusion. The "fused iridium" is plainly, as might be expected, a phosphide; and the percentage of phosphorus indicates a compound having the formula  $\text{Ir}_2\text{P}$ . For this formula the percentage of phosphorus should be 7.43, and evidence in its favor will appear farther on. Of course the product is far from pure, containing the phosphides of the other metals of the group; but its general nature is evident. With pure iridium as the starting point, a pure  $\text{Ir}_2\text{P}$  would probably be obtained.

Since it seemed desirable to ascertain how platinum would behave when treated like the iridium, experiments in that direction were undertaken. The metal used was a worn-out platinum crucible, carefully cleaned, of which a sample was first analysed. The results were as follows:

Platinum,	97.22
Iridium,	2.49
Copper,	.46
Palladium,	a trace
	<hr/>
	100.17

15.4200 grams of this material were heated to whiteness in a hessian crucible, and 20 grams of stick phosphorus were thrown in. Fusion at once took place, and when the excess of phosphorus had burned off, the mass was allowed to cool. We thus obtained a brilliant, silver white, brittle button, weighing 19.4663 grams. As it was porous, we did not determine its specific gravity. If we reckon the iridium in the mass as platinum, and ignore the trifling amount of copper, the increase in weight gives us synthetically the following composition for the product:

	Found.	Calculated for $\text{Pt}_3\text{P}_5$ .
Platinum,	79.21	79.05
Phosphorus,	20.79	20.95
	100.00	100.00

These figures are useful only in confirmation of our subsequent analyses.

A portion of the phosphide, coarsely powdered, was next boiled for at least forty hours with aqua regia. At the end of that time a considerable portion was still undissolved, and trial showed it to be quite insoluble in the reagent. The soluble portion amounted to 71.21 per cent. of the whole, and the insoluble part to 28.79 per cent. The latter, dissolved by fusion with sodium nitrate and caustic soda and subsequent boiling with aqua regia, was analysed separately, and proved to be a definite phosphide of the formula  $\text{PtP}$ .

	Found.	Calculated for $\text{PtP}$ .
Platinum,	86.16	86.28
Phosphorus,	14.03	13.72
	100.19	100.00

The soluble fraction, also analysed independently, agreed approximately with the formula  $\text{PtP}_2$ .

	Found.	Calculated for $\text{PtP}_2$ .
Platinum,	76.62	75.88
Phosphorus,	23.68	24.12
	100.30	100.00

Recalculating the analyses of the two fractions so as to express the composition of the original phosphide, we get the following results to compare with those obtained by synthesis.

	Found, analysis.	Found, synthesis.	Calculated for $\text{Pt}_3\text{P}_5$ .
Pt,	79.39	79.21	79.05
P,	20.87	20.79	20.95
	100.26	100.00	100.00

The data for the foregoing calculations, in weights, are as follows: Weight of sample, 2.2042 grams. Dissolved, 1.5695 gram; undissolved, .6347 gram. Platinum in the soluble portion, 1.2025 gram; in the insoluble, .5475 gram; total, 1.7500 gram. Phosphorus in the soluble portion (calculated from weight of  $\text{Mg}_2\text{P}_2\text{O}_7$ ), .3717 gram; in the insoluble, .0891 gram; total, .4608 gram. These figures further show that the ratio between the dissolved and insoluble phosphides agrees well with the equation  $\text{Pt}_3\text{P}_5 = \text{PtP} + 2\text{PtP}_2$ .

	Found.	Calculated.
Insoluble PtP,	28.79	30.54
Soluble $\text{PtP}_2$ ,	71.21	69.46
	100.00	100.00

The slight discordance here, 1.75 per cent., taken together with the fact that the platinum in the soluble part came out rather too high, shows that a trifling quantity of the PtP was dissolved by the very prolonged action of the aqua regia to which it had been subjected. In other words, the fractionation of the  $\text{Pt}_3\text{P}_5$  into the two simpler phosphides is not quite perfect.

In order to determine whether the complex phosphide  $\text{Pt}_3\text{P}_5$  could be reduced to metal by long heating, two portions were roasted in a muffle until constant weight was obtained. The losses in weight were 14.08 and 13.78 per cent. respectively. The product of this roasting was malleable, and readily soluble in aqua regia. It contained 7.36 per cent. of phosphorus, which is just the amount required by the formula  $\text{Pt}_2\text{P}$ . Here then we have a fourth phosphide analogous in composition to the fused iridium, and confirmatory of the formula assigned to the latter. The reduction of  $\text{Pt}_3\text{P}_5$  to  $\text{Pt}_2\text{P}$  should require a loss of 14.66 per cent. In all of these calculations we have taken 195 for the atomic weight of platinum. The trace of copper in the original platinum did not show itself in any of the analyses of the phosphides, and the small amount of iridium present could nowhere affect our results by more than a hundredth of a per cent.

In conclusion, our experiments show the existence of three simple phosphides of platinum,  $\text{PtP}_2$ ,  $\text{PtP}$ , and  $\text{Pt}_2\text{P}$ , and of a double phosphide  $\text{Pt}_3\text{P}_5$ . Of these compounds the monophosphide, by virtue of its insolubility in aqua regia, is the most noteworthy. The compound  $\text{PtP}_2$  is probably identical with the phosphide described by Schrötter,<sup>1</sup> who obtained it, as well as analogous phosphides of iridium and palladium, by heating the finely divided metal in phosphorus vapor. As far as we can learn, no other platinic phosphides have ever been regularly analysed. Pelletier<sup>2</sup> heated platinum with phosphorus and found that 300 grains of the former took up 54 of the latter; results which approximate roughly to the ratio  $\text{PtP}$ . Edmund Davy<sup>3</sup> tried two sets of experiments in the same direction. First, he heated ammonium chloroplatinate with phosphorus, and obtained a black compound of doubtful composition. Afterwards he heated platinum and phosphorus together in a vacuum, and obtained results which, calculated synthetically, agree well with the formula  $\text{Pt}_3\text{P}_4$ . This product was insoluble in strong acids, and at the time (1812) could not be directly analysed.

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## XXVIII.—ON CADMIUM IODIDE.

BY F. W. CLARKE AND E. A. KEBLER.

Of late years the suggestion has repeatedly been made, by various chemists, that the definite series of related chemical elements may be analogous in character to series of compounds such as the hydrocarbons. For example, fluorine, chlorine, bromine, and iodine form one such series; the nitrogen group, from nitrogen to bismuth, forms another, etc. There have been many efforts to trace relationships between the atomic weights in these and other similar series, and so to get evidence in favor of the foregoing hypothesis; but except in the establishment of the periodic law, all such attempts seem to have ended fruitlessly.

But notwithstanding the failure to discover definite numerical relations between the elements, the evolutionary speculation is suggestive. If the series of elements are developed progressively, like

<sup>1</sup> Sitzungsberichte Wien Akad. 1849, 301.

<sup>2</sup> Ann. de Chimie, 13, 1792, 101–143.

<sup>3</sup> Tilloch's Mag. 40, 1812, 27–39. Schweigg. Journ. 10, 382.

series of compounds, there should be various points of comparison ; and one line of thought is as follows. In any series of compounds, the possibility of isomerism increases as we ascend ; and therefore, by analogy, we should expect to find a similar state of affairs among the so-called elements. The derivatives of the highest member of a series should be more numerous and complex than those of lower members, and cases of allotropy or isomerism ought also to be more frequent. Whether this is so or not in all known instances we do not attempt to say ; our experiments bear upon a single point, and that may be stated briefly.

It is a well-known fact that allotropy is common among the metallic iodides, and much more so than among the corresponding compounds of chlorine and bromine. For example, the scarlet and yellow modifications of mercuric iodide, and the three varieties of antimony iodide may be cited. We have been engaged in the study of several other iodides, especially that of cadmium, and in this case we are now prepared to announce the existence of two distinct modifications. So far then our results lend countenance to the speculative idea which we began by quoting, even though much weightier evidence would be needed to put it upon the basis of a clear and definite theory. The speculation, however, instigated our experiments, and in their success its utility as a means of stimulating research is justified.

Up to the present time but two determinations of the specific gravity of cadmium iodide have been published. First, by Bödeker, who found it to be 4.576 at  $10^{\circ}$ ; and second, by Fullerton, whose mean result was 5.9798. The latter determination was made some years ago in this laboratory, and is undoubtedly too high ; but the discordance between the two is so great that it could hardly be ascribed to error. Accordingly, we prepared cadmium iodide by a variety of methods, and obtained the following determinations of specific gravity. All weighings were made in benzene, and the results are referred to water at  $4^{\circ}$  as unity. Our mean figures may be stated first, and the details given later.

A. Cadmium and iodine, in equivalent quantities, were heated together in a sealed tube from which the air had been exhausted. The product was white, and contained 1.30 per cent. of residue insoluble in water. Its character was established by analysis, and we found it to contain about 98.5 per cent. true  $\text{CdI}_2$ . Sp. g. 5.543.

B. Cadmium and iodine were digested together under water.

The crystals obtained by evaporation were carefully identified as  $\text{CdI}_2$ . Sp. g. 5.622.

C. A very fine sample of iodide prepared by Schuchardt, of Goerlitz, was examined. Its mode of preparation, as stated in a letter from the maker, consisted in dissolving together equivalent quantities of cadmium sulphate and potassium iodide, evaporating to dryness, extracting with alcohol and crystallising. Sp. g. 5.660.

D. Preparations A and B were mixed and recrystallised from alcohol. The sp. g., as determined by Mr. E. Twitchell, was 5.701.

So far at least the variations in our results were not startling. Our next series came out differently.

E. Cadmium carbonate was dissolved in hydriodic acid. The solution, discolored by free iodine, was rendered nearly colorless by cadmium clippings, and crystallised. Sp. g. 4.612. A second series of determinations gave 4.596. Both figures agree well with Bödeker. The salt was analysed, with results as follows :

	Found.	Calculated for $\text{CdI}_2$ .
Cadmium,	30.40	30.60
Iodine,	69.33	69.40
	99.73	100.00

F. To verify these results, if possible, another lot of iodide was prepared with carbonate and acid, but the solution was not decolorised by metal. Sp. g. 5.729. The sample on analysis yielded 30.56 per cent. of cadmium.

G. Another solution was prepared as under F, and divided into two parts. One was allowed to evaporate spontaneously at a low temperature. Sp. g. of product 5.610.

H. The second part of solution G was boiled down rapidly. Sp. g. of iodide 5.675.

I. Metallic cadmium was dissolved in hydriodic acid. The solution yielded a pure iodide of sp. g. 4.688, as determined by Mr. Twitchell. This preparation dried at  $50^\circ$ , became silver grey and its sp. g. rose to 5.141. Again heated to  $50^\circ$  the sp. g. rose to 5.536. A third heating brought it up to 5.545. Accompanying this change there was a little decomposition which resulted in the formation of a trifling amount of insoluble material.

The foregoing results all point pretty definitely to the existence of two allotropic varieties of cadmium iodide, differing in specific gravity by about a unit. The higher density represents a union of cadmium and iodine with little or no change of volume, while the lower corresponds to a noteworthy expansion and consequent instability. The higher or normal salt, which we may call  $\alpha$  cadmium iodide, is white, and undergoes no perceptible change when heated to any temperature below  $250^\circ$ . The lower or  $\beta$  salt is brownish, and loses weight even at  $40^\circ$ . One sample lost 5.50 per cent. at  $50^\circ$ , an alteration which is undoubtedly due to the formation of an oxide or oxyiodide with liberation of iodine. The increase in specific gravity upon heating may be partly due to the same change, but is mainly ascribable to a transformation of the  $\beta$  into the  $\alpha$  modification. The conditions governing the formation of the new salt are obscure and need farther study. In our experiments we obtained it only twice, and in each case cadmium was acted upon by hydriodic acid. In the first instance, however, this action was only incidental to the decolorisation of a solution of iodide otherwise prepared, and was necessarily very trifling. In both cases, however, cadmium iodide was exposed to the action of nascent hydrogen, and it is probable that the latter had something to do with the production of the  $\beta$  compound. This suggestion we offer merely as a clue for use in further study, without any speculations as to just how the reactions proceeded.

In detail, our specific gravity determinations were as follows, including the temperatures of weighing. The series are lettered as before :

### I. *The normal CdI<sub>2</sub>.*

A.	B.	C.	D.
5.539, 20.4°	5.622, 15.2°	5.697, 17.5°	5.716, 14.8°
5.530, 20.1	5.618, 15.2	5.704, 18.	5.714, 15.3
5.530, 20.1	5.638, 15.2	5.630, 18.2	5.696, 15.5
5.574, 20.2	5.629, 15.4	5.650, 18.1	5.696, 15.8
5.543, 19.9	5.630, 15.6	5.642, 18.2	5.685, 15.9
5.543, 19.9	5.621, 16.1	5.626, 18.2	
5.523, 19.8	5.610, 16.6	5.672, 18.2	
5.564, 20.1	5.611, 16.6		
5.543	5.622	5.660	5.701

F.	G.	H.
5.750, 10.5°	5.580, 17.6°	5.682, 15.0°
5.740, 10.5	5.610, 17.4	5.654, 15.2
5.715, 10.6	5.660, 17.7	5.683, 15.1
5.747, 10.5		5.682, 15.0
5.719, 10.6		
5.705, 10.6		
5.729	5.610	5.675
Total, 41 weighings.	Mean of all, 5.644.	

II.  $\beta$  CdI<sub>2</sub>.

E <sub>1</sub> .	E <sub>2</sub> .	I.
4.618, 14.0°	4.598, 15.2°	4.697, 18.8°
4.607, 14.4	4.594, 15.3	4.713, 18.9
4.609, 14.7	4.601, 15.2	4.740, 19.0
4.618, 15.0	4.602, 15.2	4.668, 19.0
4.612, 15.1	4.592, 15.4	4.625, 18.9
4.615, 15.1	4.593, 15.4	
4.605, 15.2	4.595, 15.2	
4.612	4.596	4.688

Total, 19 weighings. Mean of all, 4.626.

Molecular volume,  $\alpha$  salt, 64.8 $\text{``}$   $\text{``}$   $\beta$   $\text{``}$  79.2

Mol. vol. Cd + I<sub>2</sub>, 64.3, when sp. g. iodine = 4.948 (Gay Lussac), and sp. g. Cd = 8.655 (Matthiessen).

In connection with these experiments a little work was done upon the double iodides of cadmium. Attempts were made to prepare such double salts with the iodides of lead and of thallium, but unsuccessfully. Mercuric iodide dissolved freely in a hot solution of cadmium iodide, and the liquid, upon cooling, deposited scarlet crystals of the first-named salt unaltered. The mother liquor from these crystals, upon longer standing, yielded golden laminae, which were recrystallisable from hot alcohol. They were anhydrous, and contained iodine, cadmium and mercury. A partial analysis pointed to the formula CdI<sub>2</sub>.3HgI<sub>2</sub>.

	Found.	Calculated.
Cadmium,	6.90	6.48
Iodine,	58.80	58.98
Mercury,	34.30 by difference.	34.54
	100.00	100.00

There was not enough of this salt to admit of further investigation.

With other iodides we have not yet gone very far. Zinc iodide, prepared by direct union of the elements and sublimation in a stream of carbon dioxide, has a sp. gr. of 4.666.<sup>1</sup> Bödeker found a sp. gr. of 4.696. For a somewhat impure bismuth iodide from Schuchardt we found the sp. gr. to be 5.548. Bödeker's value was 5.652.

With stannic iodide we are still engaged. Suffice it to say that we are satisfied of the existence of at least two modifications, one darker red and less soluble in benzene than the other. But the difficulty of obtaining pure and definite products is very great, and we may not have time to complete the investigation.

## XXIX.—SOME SPECIFIC GRAVITY DETERMINATIONS

BY F. W. CLARKE.

The following specific gravity determinations were made under my supervision by the students named below. The salts were weighed in benzene, and the density of water at 4° was taken as unity. Each figure is the mean of several closely concordant results.

Uranyl sulphate,  $(\text{UO}_2)\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , 3.280 at 16.5°. H. Schmidt.

Uranyl ammonium sulphate,  $(\text{UO}_2)\text{Am}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , 3.0131 at 21.5°. H. Schmidt.

Uranyl potassium sulphate,  $(\text{UO}_2)\text{K}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , 3.363 at 19.1°.

H. Schmidt.

Double salt,  $\text{K}_2\text{CrO}_4 \cdot 2\text{Hg}(\text{CN})_2$ , 3.564 at 21.8°. H. Schmidt.

Ferric chloride, sublimed,  $\text{Fe}_2\text{Cl}_6$ , 2.804 at 10.8°. J. P. Grabfield.

Ferrous "  $\text{Fe Cl}_2$ , 2.988 at 17.9°. J. P. Grabfield.

Chromic " violet,  $\text{Cr}_2\text{Cl}_6$ , 2.757 at 15°. J. P. Grabfield.

Chromous"  $\text{CrCl}_2$ , 2.751 at 14°. J. P. Grabfield.

The last compound contained 14 per cent. of chromic oxide as an impurity, and the sp. gr. actually found was 3.067. This, corrected by means of Schröder's value for  $\text{Cr}_2\text{O}_3$ , 5.01, gives the sp. gr. assigned above.

<sup>1</sup> Value actually found, 4.736. This was corrected for 3.13 per cent. of admixed metal, becoming 4.666. There were six concordant estimations.

- Strontium chloride, cryst.,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ , 1.964, 16.7°. E. Muehlberg.
- Cadmium chloride,  $\text{CdCl}_2$ , 3.655, 16.9°. P. A. Knight.
- " bromide,  $\text{CdBr}_2$ , 4.794, 19.9°. "
- " fluoride,  $\text{CdF}_2$ , 5.994, 22.0°. E. A. Kebler.
- Thallium iodide, precipitated,  $\text{TlI}$ , 7.072, 15.5°. E. Twitchell.
- " " after fusion,  $\text{TlI}$ , 7.0975, 14.7°. E. Twitchell.
- " bromide, precipitated,  $\text{TlBr}$ , 7.540, 21.7°. H. Keck.
- " " after fusion, " 7.557, 17.3°. "
- Lead bromide, precipitated,  $\text{PbBr}_2$ , 6.572, 19.2°. "
- Silver tartrantimonite,  $\text{SbAgC}_4\text{H}_4\text{O}_5$ , 3.4805, 18.2°. C. S. Evans.

### XXX.—RESEARCHES ON THE TARTRATES OF ANTIMONY.

BY F. W. CLARKE AND CHARLES SETH EVANS.

Although some of the double tartrates of antimony, such as the tartar emetics, have been quite elaborately studied, our knowledge of its simple tartrates has hitherto been singularly inexact and vague. According to Bergmann,<sup>1</sup> a solution of antimonious oxide in aqueous tartaric acid crystallises confusedly; while according to Dulk<sup>2</sup> it does not crystallise at all. Berzelius<sup>3</sup> and Peligot<sup>4</sup> both obtained large crystals, but assigned different formulæ; Berzelius without analysis, Peligot after investigation. Peligot, however, must have calculated his formula upon the basis of  $\text{Sb}=129$ , the old Berzelian determination; and his analysis, recalculated with the modern value of  $\text{Sb}=120$ , leads to no intelligible symbol. The precipitate formed by alcohol in solutions of the crystalline tartrate was also examined by Berzelius and by Peligot; and here again, upon incomplete analyses, different formulæ were based. In short, neither Berzelius nor Peligot studied these compounds at all thoroughly; and the subject, up to the time when we began our own experiments, was in a most confused state. Inferences were more numerous than facts, and the latter needed scrupulous reverification. We believe that we have succeeded in shedding some light upon the nature of the substances in question; and that

<sup>1</sup> See Gmelin's Handbook, edition of the Cavendish Society, **10**, 297.

<sup>2</sup> Lehrbuch, 5 Aufl. **3**, 1124.

<sup>3</sup> Annales de Chim. et de Phys. 3 série, **20**, 289.

the results which we have obtained may form a fair basis upon which to conduct future investigations.

Antimony trioxide, as is well known, is readily soluble in aqueous tartaric acid; but the properties of the solution depend upon the relative proportions of its constituents. When the oxide is dissolved in the acid to complete saturation, the solution yields no crystals whatever; but upon evaporation dries up to a gummy, amorphous mass. With less oxide and an excess of acid, crystallisation becomes possible, and in every case of this kind, rosettes of needles are obtained. If the acid is in slight excess, crystallisation takes place with difficulty, and the smaller the proportion of the oxide the more easily the crystals form. In all cases, however, in which the crystallisation occurs, the mother liquors are exceedingly viscous and consequently difficult to remove; so that it is by no means easy to secure pure products for examination. Furthermore, the crystals vary in composition, as the following percentages of antimony will show:

1. 40 grams of  $Sb_2O_3$  were boiled with 60 grams of tartaric acid. The solution was incomplete. The filtered liquid, evaporated to dryness, gave a product containing 27.53 per cent. of antimony.

2. 35 grams  $Sb_2O_3$  to 60 of acid. Yielded indistinct crystals which could not be purified for analysis.

3. 30 grams  $Sb_2O_3$  to 60 of acid. Crystals washed and twice recrystallised. Per cent. of Sb, 18.92.

4. 20 grams  $Sb_2O_3$  to 60 of acid. Product recrystallised. Several distinct lots of material gave crystals containing antimony in the following percentages:

A	13.35			
B	15.90			
C	16.48	16.64		
D	16.18	16.21	17.16	
E	17.88	18.00		

The last product was dried with extreme care and examined further. The results will be given later.

5. 15 grams  $Sb_2O_3$  to 60 of acid. Product recrystallised. Per cent. of Sb, 5.37. Probably a mixture.

6. 12 grams  $Sb_2O_3$  to 60 of acid. Per cent. of antimony in crystals, 3.69 to 3.82. Probably a mixture.

The antimony was weighed as sulphide in every case, and the results indicate two things: First, the difficulty of obtaining definite products; and second, the probable existence of a series of salts. Two of the latter were analysed, as follows:

*First.* The crystals marked 3 and the preparation 4 E. of the foregoing table had all the characteristics of definite compounds. They proved to be identical, and to be closely represented by the formula  $\text{Sb}(\text{C}_4\text{H}_4\text{O}_6)_3\text{H}_2\text{O}$ .

	Found.	4 E.	Calculated.
Sb	18.92 <sup>3.</sup>	17.88	18.78
C	22.59	22.98	22.53
H	3.78	3.39	3.60
Water at 120°	11.05	10.98	11.27

In brief, this tartrate, which may fairly be called antimonio-tri-tartaric acid, is simply a triple molecule of tartaric acid with half its replaceable hydrogen replaced by an atom of trivalent antimony. It crystallises in rosettes of white needles and is easily soluble in water. With carbonates it effervesces strongly and behaves like a weak acid. Its reactions in this particular will be considered further on. With alcohol its solution yields a copious white precipitate, which, washed with alcohol and thoroughly dried over sulphuric acid, proved to be neutral antimonious tartrate,  $\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_3\cdot 6\text{H}_2\text{O}$ .

	Found.	Calculated.
Sb	30.58	30.30
C	18.14	18.18
H	3.01	3.03
Water at 160°	13.86	13.63

This salt is easily soluble in water. In its cold solution sodium carbonate produces no turbidity; but, upon heating, a copious white precipitate is thrown down. This particular precipitate we did not examine more closely, but its nature may be inferred from evidence to be cited later. It undoubtedly consists either of basic mixtures or of antimonious oxide, according to the amount of sodium carbonate used and the thoroughness of the boiling.

Attempts were made to prepare definite salts of antimonio-tri-tartaric acid, but unsuccessfully. Barium carbonate dissolves in a solution of the acid with brisk effervescence, but, upon standing, crystals of ordinary barium tartrate were deposited. The anti-

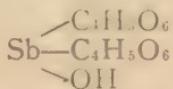
mony in this case remained dissolved undoubtedly as the normal tritartrate. In another experiment a solution of the acid was rapidly neutralised with barium carbonate, and subsequently precipitated by alcohol. The copious white precipitate was washed with alcohol, air dried, and partially analysed. So far as ascertained its composition agrees with the formula  $\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 4\text{BaC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ . It is probably a mixture.

	Found.	Calculated.
Sb	12.47	12.77
Ba	28.27 29.06	29.17
Water at 150°	2.45	2.87

*Second.* It has already been stated that a saturated solution of antimonious oxide in tartaric acid does not crystallise. Such a solution (marked 1 in the previous table) was evaporated to dryness and the dry product was analysed. The results were as follows:

Sb	27.53
C	18.31
H	2.96
$\text{H}_2\text{O}$ at 105°	10.92

This analysis is of dubious value. The compound may not have been definite, and the figures agree sharply with no probable formula. The antimony and carbon give a ratio corresponding to seven molecules of acid to four atoms of metal, and suggest the existence of a compound having the formula  $\text{Sb}(\text{OH})\text{H}_2(\text{C}_4\text{H}_4\text{O}_6)_7$ . Such a formula, which may be written structurally



is also indicated by Peligot's analysis of his "hyperacid tartrate," but it is not clearly proved. It is also further suggested by the following reaction:

A solution containing the foregoing salt was mixed with alcohol. The usual white precipitate was washed with alcohol and air-dried over sulphuric acid. Its composition is clearly represented by the formula  $\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2\text{O} \cdot 6\text{H}_2\text{O}$ :

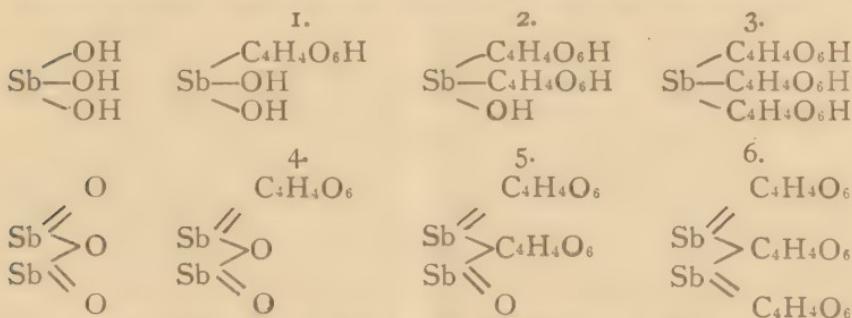
	Found.	Calculated.
Sb	36.88 36.22	36.58 36.37
C	13.56 13.90	13.56 14.54
H	2.65 2.72	2.47 3.03
$\text{H}_2\text{O}$ at 155°	16.31 ...	... 16.36

A portion of this was redissolved in water, and the solution was left to evaporate. No crystals formed, but the liquid dried up to a yellowish, scaly mass, containing 16.39 per cent. of water. Evidently no change in composition had occurred. Heated to 170° the salt lost another molecule of water, leaving two molecules of  $\text{Sb} \equiv \text{C}_4\text{H}_3\text{O}_6$ .

Actual loss at 170°, 19.28 per cent. Theoretical, 19.09.

A similar precipitate was also examined by Peligot, who dried his product at 160° and estimated only carbon and hydrogen. From his results the formula  $\text{SbC}_4\text{H}_3\text{O}_6$  has been inferred, as well as the existence of an acid salt  $\text{SbC}_4\text{H}_3\text{O}_7$ .<sup>1</sup> The latter compound, however, he never actually obtained; and the only evidence of its existence and properties was published from this laboratory some four years ago.<sup>2</sup>

If now we compare the formulae of our two acid salts (using our hypothetical formula for the second) with those of the two alcoholic precipitates, certain obvious relations will appear. There ought plainly to be two series of antimony tartrates, one acid and one neutral; the first derived from orthoantimonious acid,  $\text{Sb}(\text{OH})_3$ , and the other from antimonious oxide,  $\text{Sb}_2\text{O}_3$ . The formulae should be as follows, neglecting water of crystallization:



Of these, numbers 3, 5 and 6 we have actually obtained in definite condition, and number 2 we have shown to be probable. The latter is related to the neutral ditartrate just as antimonio-tritartaric acid is related to the tritartrate, and the name of antimonio-ditartric acid may fitly be applied to it. By precipitation with alcohol it yields a neutral ditartrate, precisely as number 3 by a similar reaction yields number 6. The formula, doubled, and with five molecules of water added, is found in all reference works upon chemistry as that of Peligot's hyperacid tartrate.

<sup>1</sup> Commonly written  $\text{C}_4\text{H}_4\text{H}(\text{SbO})\text{O}_6$ .

<sup>2</sup> Clarke and Stallo, this Journal, 2, 319.

The hypothetical compound numbered 1 in the foregoing schedule we did not obtain. Number 4, the monotartrate, we attempted to investigate, but with only partial success. After a number of failures, which resulted in the formation of the neutral ditartrate, we prepared a quantity of antimonious hydroxide, which we dissolved to saturation in aqueous tartaric acid. This solution yielded a precipitate with alcohol which was comparatively insoluble in water, and which, air-dried, had the subjoined composition :

	Found.	Calculated for $Sb_2(C_4H_4O_6)O_2 \cdot 2H_2O$ .
Sb	53.62	53.84
C	6.43	5.38
H	1.65	1.51
$H_2O$ at $160^\circ$	7.79	7.89

It will at once be seen that the analysis, though suggestive, is highly unsatisfactory. It merely emphasises the probability that the compound sought for exists. The white precipitate described by Berzelius had similar properties as regards insolubility, and his formula for it, translated into modern notation, agrees with ours. On the antimonyl hypothesis its formula is found in works of reference as  $C_4H_4(SbO)_2O_6$ . It needs, however, further investigation.

In all essential particulars the salt which we call antimonio-ditartaric acid behaves much like the corresponding tri-compound. It is strongly acid, effervesces with carbonates, and is not precipitated by alkalies in the cold. Its solution, saturated with barium carbonate and precipitated by alcohol, behaved precisely like that of the tri-acid, but the curdy white precipitate had a different composition. A partial analysis gave results agreeing with  $Sb_2(C_4H_4O_6)_2O_3BaC_4H_4O_6 \cdot 11H_2O$ .

	Found.	Calculated.
Sb	15.33	14.94
Ba	26.06	25.58
$H_2O$ at $150^\circ$	12.66	12.32

This too is most probably a mixture, although both it and the corresponding tri-acid precipitate may be weak double compounds.

In order to get further evidence concerning the nature of the acid compounds, we neutralised a solution of the di-acid with sodium carbonate. The liquid, which remained perfectly clear,

was then mixed with alcohol. At first it became turbid, and later it separated into two fluid layers, both clear, and both containing antimony. The lower layer was syrupy, and contained most of the sodium; it was accordingly drawn off, and evaporated at the ordinary temperature of the air over sulphuric acid. It slowly dried up to an amorphous, gummy mass, which yielded a yellowish powder. This product we analysed. Although, under the circumstances, we could hardly expect a definite compound, our figures approximate to what is required by the empirical formula,  $2\text{Sb}(\text{OH})_3 \cdot 3\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ .

	Found.		Calculated.
Sb	24.66	25.00	24.54
Na	13.48		14.11
C	15.64	15.77	14.72
H	2.62		2.45
$\text{H}_2\text{O}$ at $150^\circ$	11.66		11.04

This compound is probably definite, although we may have failed to determine exactly the right formula. It is readily soluble in water, and very faintly acid towards litmus paper. Its solution is stable even upon boiling, but is precipitated, when hot, by alkaline carbonates.

Another portion of the antimonio-ditartaric acid solution was exactly neutralised by sodium carbonate and boiled. A heavy precipitate fell, which we collected and dried over sulphuric acid. To the filtrate more sodium carbonate was added, and a second boiling threw down a second precipitate. Both precipitates, 1 and 2, were analysed.

	I.	II.
Sb	47.87	47.28
C	3.96	4.24
H	3.44	3.21
$\text{H}_2\text{O}$ , $155^\circ$	22.30	4.80

The second product is evidently antimonious oxide mixed with a little hydrate. The pure oxide contains 83.33 per cent. of metal. The first precipitate approximates roughly to a tartrate having the formula  $\text{Sb}_4\text{O}_5(\text{C}_4\text{H}_4\text{O}_6) \cdot 12\text{H}_2\text{O}$ , analogous to the sulphate  $\text{Sb}_4\text{O}_5(\text{SO}_4)$ , the chloride  $\text{Sb}_4\text{O}_5\text{Cl}_2$ , etc. Doubtless such a tartrate exists, and might be prepared in a state of purity by proper precautions. It should contain 51.95 per cent. Sb, 5.20 per cent. C,

3.03 per cent. H, 23.37 per cent. H<sub>2</sub>O. Our results, however, only indicate the probability of such a basic salt, formed by the partial precipitation of the higher tartrates, as a step in the reduction of the latter to oxide.

With the neutral<sup>1</sup> ditartrate of antimony one more suggestive experiment was tried. Its solution was cautiously mixed with dilute sulphuric acid to incipient turbidity, and then immediately precipitated by alcohol. The precipitate, which was white, contained sulphuric and tartaric acids, antimony and water.

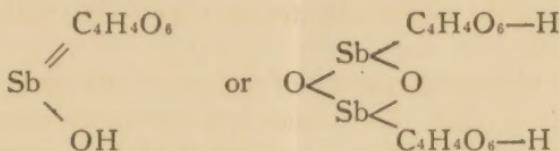
	Found.
Sb	33.56
SO <sub>4</sub>	25.48      25.52
H <sub>2</sub> O at 110°	12.31

A compound having the formula Sb<sub>2</sub>(C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>)(SO<sub>4</sub>)<sub>2</sub>.7H<sub>2</sub>O, would require 33.99 per cent. Sb, 27.19 per cent. SO<sub>4</sub>, and 17.84 per cent. H<sub>2</sub>O. A loss of 5H<sub>2</sub>O would amount to 12.75 per cent. Our figures, however, here as in several other cases, are merely sufficient to establish a probability which may serve as a basis for future investigations. It may be regarded as practically certain that mixed salts of antimony are possible, and that sulphato-tartrates, etc., may be obtained by careful and systematic trial. Want of time precluded us from working farther in this direction.

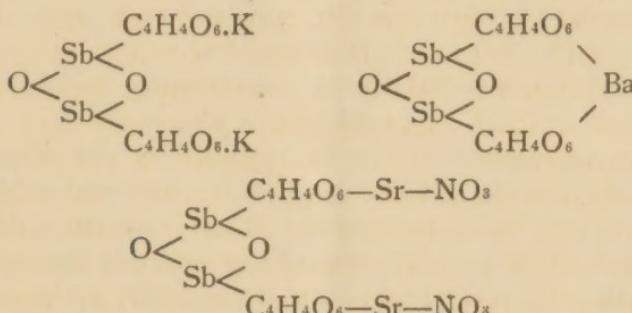
The foregoing results, taken altogether, establish certain points pretty clearly. First, contrary to Peligot's views, antimony forms perfectly normal tartrates, in which it acts like any other trivalent metal, and in which the assumption of an antimonyl radicle, SbO, is entirely inadmissible. The other tartrates of antimony fall naturally into series, in which we sometimes find the atoms Sb and O united in accordance with Peligot's hypothesis, but not in such a way as to give the latter any validity. In all such cases the SbO group is not to be regarded as a distinct radicle, but rather as an incident in a series; a mode of union found in many other basic compounds of other metals for which no special explanation has ever been thought necessary. In the tartar emetics we have a set of salts which may or may not be interpreted on the antimonyl theory, as was shown in this laboratory some years ago, but which are best explained by regarding them as derived from a complex

<sup>1</sup> The word "neutral" is inexact, but serves provisionally to indicate those tartrates of antimony which contain no replaceable hydrogen. Some of them are really basic.

tartrantimonious acid, to which may be assigned either of the two formulæ given below :



The first formula was adopted in the paper from this laboratory which we previously cited, but the latter is suggested by the fact that tartar emetic, as usually written, contains only half a molecule of water, and that therefore its formula should be doubled. On this plan the tartar emetics of barium and potassium may be formulated as below, and Kessler's double salt of strontium tartar emetic and strontium nitrate becomes easily explainable also.



In the course of our present investigation we have done some work upon this class of compounds, and notably as follows : A quantity of silver tartar emetic was dissolved in boiling water and precipitated by the addition of amyl iodide. Silver iodide was thrown down, the solution was instantly filtered, and upon cooling white brilliant crystals were deposited. These were insoluble in water and too small for us to determine their form. Analysis gave a composition best represented by the empirical formula  $2\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)\text{O}_2 \cdot \text{Ag}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ .

	Found.		Calculated.
Sb	37.37	38.54	38.15
Ag		17.19	17.17
C	11.21	11.26	11.45
H	1.15	1.21	1.42
$\text{H}_2\text{O}$ , at $150^\circ$		3.43	4.29

Although the agreement here is very close, and the preparation of the salt, repeated several times, gave a perfectly uniform and apparently definite product, the formula cannot be regarded as certain. Our difficulty is that a similar experiment with ethyl iodide gave a salt of similar appearance but of different composition, as follows :

Sb	33.37
Ag	21.61
C	11.86
H	1.16
H <sub>2</sub> O	4.44

Possibly this preparation, which we made only once, contained unaltered silver tartar emetic. At all events, uncertainty exists, and further investigation is necessary. If the formula given above should prove to be correct it would relate the compound structurally to the salts Sb<sub>4</sub>O<sub>5</sub>Cl<sub>2</sub>, Sb<sub>4</sub>O<sub>5</sub>(SO<sub>4</sub>), etc.

In conclusion, we may describe the following new tartrantimonites :

Aniline tartrantimonite, SbC<sub>4</sub>H<sub>5</sub>O<sub>7</sub>.C<sub>6</sub>H<sub>7</sub>N, was obtained by treating the barium salt with a solution of aniline sulphate. It crystallises very easily in long white prisms, sometimes discolored by traces of oxidation products, and has a specific gravity of 1.890 at 11°. It yielded 31.74 per cent. of antimony, which is exactly the theoretical amount.

The quinine and atropine tartar emetics were prepared in a similar manner by Mr. Karl W. Langenbeck. Both salts were amorphous, yellowish, translucent masses. The quinine salt was anhydrous ; the atropine salt contained two molecules of water. The analytical data are subjoined :

Quinine Salt.	Found.	Calculated.
Sb	19.63	19.76
		19.70
Atropine Salt.	Found.	Calculated.
Sb	19.88	19.67
H <sub>2</sub> O	5.62	5.90